



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material 2694a

#### Simulated Rainwater

This Standard Reference Material (SRM) has been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. SRM 2694a consists of four 50 mL solutions, two at each level, in polyethylene bottles. It was prepared by the dissolution of high-purity salts and acids in high-purity distilled/deionized water.

Certified values and methods used for certification are given in Table 1. Values in parentheses are *not* certified, but are included for information only and are given as additional information on the matrix. The information values are not certifiable because of instability of the constituent concentration or only one method was used in the certification protocol. The nitrate concentration in 2694a-I and the ammonium concentration in 2694a-I and 2694a-II are unstable. The cause of the instability is not known at this time and it does not appear to significantly affect any other component in the solutions. The chloride concentration was measured using only one NIST technique and consequently does not meet the NIST requirement for certification.

Transition and heavy metals are not included in SRM 2694a as they are not stable in solutions at this pH level.

**Expiration of Certification:** The data included on this Certificate of Analysis are valid for 12 months from the date of purchase and shipment from NIST.

**Precautions:** The solutions of SRM 2694a are very dilute, unbuffered, and as such are very susceptible to contamination. Therefore, the solutions should be used immediately upon opening. No assurances can be made as to the composition or stability of the solutions after being opened and recapped. SRM 2694a should be stored in an area free from acid and/or ammonia fumes or vapors. Refrigeration of the solutions is not necessary, however, they should not be exposed to extreme heat.

**Additional Information:** If conductivity and pH are to be measured on the same sample, then conductivity must be measured first to prevent leakage from the pH reference electrode filling solution. The measurement of pH should be performed according to the guidelines set forth in the attachment to this document to minimize the bias caused by residual liquid junction potentials. Acidimetric titrations should be performed on samples that have been purged of dissolved carbon dioxide to prevent drifting endpoints and high results. Care must be exercised in the determination of chloride and fluoride by ion chromatography to avoid possible errors associated with the negative water-dip in the baseline.

The preparation and analyses of these solutions were performed by W.F. Koch, W.R. Kelly, G.C. Turk, M.S. Epstein, T.A. Rush, L.J. Woods, Y.C. Wu, M. Sarver, P. Ewt, J.M. Smeller, A.P. Emery, K.E. Hehn, and K.W. Pratt of the NIST Analytical Chemistry Division.

Statistical analysis of the certification data was performed by R.C. Paule of the NIST Statistical Engineering Division.

Gaithersburg, MD 20899  
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(Revision of certificate dated 6-10-91)

Thomas E. Gills, Chief  
Standard Reference Materials Program

(over)

The overall direction and coordination of the technical measurements leading to the certification of this SRM were performed under the direction of W.F. Koch of the NIST Analytical Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by T.E. Gills. Revision of this certificate was coordinated through the Standard Reference Materials Program by J.S. Kane.

Table 1. Simulated Rainwater

Constituent Elements Parameters	Methods	2694a-I			2694a-II		
pH @ 25 °C	c	4.30	±	0.03	3.60	±	0.03
Electrolytic Conductivity <sup>1</sup> (PS/cm)	b	23.4	±	1.2	119.9	±	1.3
		25.4	±	1.2	129.3	±	1.3
Acidity, meq/L	d	0.0544	±	0.0006	0.283	±	0.003
Fluoride, mg/L	a,c	0.057	±	0.005	0.108	±	0.004
Chloride, mg/L	a	(0.23)			(0.94)		
Nitrate, mg/L	a,f	(0.53)			7.19	±	0.16
Sulfate, mg/L	a,e	2.69	±	0.03	10.6	±	0.1
Sodium, mg/L	a,g,h	0.208	±	0.002	0.423	±	0.012
Potassium, mg/L	a,g,h	0.056	±	0.002	0.108	±	0.003
Ammonium, mg/L	a	(0.12)			(1.06)		
Calcium, mg/L	g,i	0.0126	±	0.0014	0.0364	±	0.0006
Magnesium, mg/L	g,i,k	0.0242	±	0.0002	0.0484	±	0.0010

<sup>1</sup>The temperature coefficient for the electrolytic conductivity of both solutions in SRM 2694a has been determined experimentally to be about 1.5 percent per degree Celsius at 25 °C. The density of the solutions is 0.997 g/mL at 25 °C.

**Noncertified Values:** Noncertified values are provided for information only. An element concentration value may not be certified if a bias is suspected in one or more of the methods used for certification, or if two independent methods are not available.

*The certified values are based on proven reliable methods of analysis. The estimated uncertainties are two standard deviations of the certified values, except for uncertainties associated with pH, electrolytic conductivity and acidity which are based on scientific judgment and are roughly equivalent to two standard deviations of the certified value. A few of the very small standard deviations have been expanded to be 1% of the analyte value to allow for unavoidable minor changes in the sample.*

#### Methods:

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|--|--|
| a. Ion Chromatography                                    | f. Spectrophotometry                       |
| b. Conductimetry   | g. Laser Enhanced Ionization Spectrometry  |
| c. Potentiometry/Ton Selective Electrodes                | h. Flame Emission Spectrometry             |
| d. Coulometry  | i. Inductively Coupled Plasma Spectrometry |
| e. Isotope Dilution Thermal Ionization Mass Spectrometry | j. Flame Atomic Absorption Spectrometry    |
|  | k. Direct Current Plasma Spectrometry      |

## GUIDELINES FOR THE MEASUREMENT OF pH IN ACIDIC RAINWATER

This report presents a recommended procedure for the measurement of pH in acidic rainwater. The intent of this guideline is to improve the accuracy and precision of the pH measurement with special emphasis on reducing the effect of the residual liquid junction potential. It consists of three major parts: Calibration Sequence, Control Sequence, and Rainwater Measurement Sequence. The purposes of the Calibration Sequence are to accurately calibrate the pH measurement system with robust buffer solutions, to accurately set the slope, and to verify that the measurement system is functioning properly. The purpose of the Control Sequence is to quantitatively determine the magnitude of the residual liquid junction potential bias for a particular set of electrodes which must be applied in the rainwater measurement sequence to obtain more reliable and intercomparable results. Each sequence should be executed in stepwise order with strict adherence to detail.

**Note:** This guideline is applicable only to the measurement of pH in acidic rainwater and acidic low ionic strength aqueous solutions. It should not be used for other applications as inaccuracies may ensue.

### General Directions

Record the solution temperature to within 1 °C. Record all pH values to at least 0.01 pH unit. Make all measurements in a quiescent solution. Fully document all calibration and control standards.

### Calibration Sequence

- 1) Standardize the pH electrodes and meter using SRM 185g. Potassium Hydrogen Phthalate [pH(S) 4.005 at 25.0 °C, 0.05 molal], or equivalent. Refer to ASTM D1293, "Standard Test Methods for pH of Water" for guidance. Record the value. Rinse the electrodes with distilled water (ASTM Type II or better).
- 2) With the slope adjustment of the meter set at 100 percent, and the temperature adjustment set at the temperature of the buffer solution, check the Nernstian response of the pH measurement system with a second buffer, SRM 186Ie/186Ile, Potassium Dihydrogen Phosphate/Disodium Hydrogen Phosphate [pH(S) 6.863 at 25.0 °C], or equivalent.<sup>A</sup> Refer to ASTM D1293 for guidance. If the reading for the second buffer is not within 0.03 pH units of the prescribed value, recheck the calibration of the system.<sup>B</sup> DO NOT CONTINUE until the conditions for calibration and Nernstian response have been satisfied. If the reading for the second buffer is within 0.03 pH units of the prescribed value, record the value and continue.

### Control Sequence

- 3) Rinse the electrodes thoroughly with distilled water (ASTM Type II or better). Remove drops of water on the electrode by blotting gently (Do Not Rub!) with a clean lab tissue.
- 4) Insert the electrodes into a clean beaker (10-20 mL capacity) containing a portion (10-20 mL) of the rainwater control standard (e.g., SRM 2694a-I<sup>C</sup>). Be certain that the reference junction and glass bulb are completely immersed. Do not insert the electrodes directly into the polyethylene bottles.
- 5) Stir and swirl the solution to ensure homogeneity and contact with the electrodes.
- 6) Allow the solution to settle to a quiescent state (approx. 30 s). Record the pH after the reading has stabilized.<sup>D</sup>
- 7) Discard this portion of the control standard. Do not use for subsequent control checks or for other analytical determinations such as electrolytic conductivity, anions, cations, and acidity.
- 8) Repeat steps 3 through 7 with a second rainwater control standard (e.g., SRM 2694a-II<sup>C</sup>).
- 9) Calculate the differences between the true pH values of the rainwater control standard and the values as determined by the pH measurement system.<sup>E</sup> Average the differences and apply this bias correction to subsequent rainwater measurements. (For example, if the pH measurement system displays the pH of the control 0.13 pH units lower than the true value, add 0.13 pH units to the subsequent pH measurements of rainwater.)

## Rainwater Measurement Sequence

- 10) Rinse the electrodes thoroughly with distilled water (ASTM Type II or better). Remove drops of water on the electrode by blotting gently (Do Not Rub) with a clean lab tissue.
- 11) Insert the electrodes into a clean beaker containing a portion (10-20 mL) of the rainwater sample. Be certain that the reference junction and glass bulb are completely immersed.
- 12) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.
- 13) Allow the solution to settle to a quiescent state (approx. 30 s). Record the pH after the reading has stabilized.
- 14) Apply the bias correction as determined in step 9 and report this corrected value as the pH of the rainwater sample.
- 15) Discard this portion of the rainwater sample. Do not use it in other analytical tests.
- 16) Repeat steps 10 through 15 for subsequent rainwater samples.
- 17) Repeat the Control Sequence at regular intervals, based upon quality control guidelines, performance history of the measurement system, frequency of measurements, and required accuracy.

## Storage of Electrodes

- 18) When not in use, soak the electrodes in a solution which is 0.1 mol/L potassium chloride and  $1 \times 10^{-4}$  mol/L hydrochloric acid. Do not store the electrodes in buffers, concentrated acids, concentrated potassium chloride, basic solutions, or distilled water. Do not allow the electrodes to dry out.
- 19) Use the electrodes exclusively for rainwater measurements.

## Notes

- A) For the highest accuracy and the most direct traceability to the National Institute of Standards and Technology, it is recommended that freshly prepared solutions of Standard Reference Materials (SRMs) be used.
- B) Possible causes for deviation from Nernstian response include:
  - i) improper calibration,
  - ii) old or contaminated buffer solutions,
  - iii) insufficient rinsing of the electrodes between solutions,•
  - iv) plugged reference junction,
  - v) defective electrodes, and
  - vi) defective meter.

It may be necessary to replace the electrodes with a new pair if the non-Nernstian behavior persists even with accurately and freshly prepared buffer standards.

- C) Standard Reference Material 2694a, Simulated Rainwater, is issued by the National Institute of Standards and Technology, Standards Reference Materials Program.
- D) Some systems may require 5 min or more to stabilize. If drifting persists, record the reading after 10 min and annotate the data accordingly. With such severe drift, it would be advisable to acquire a different type of pH electrode which does not exhibit this adverse characteristic.
- E) The difference should agree to within 0.05 pH units. If not, repeat the Control Sequence.